10/576284
IAP15 Rec'd PCT/PTO 17 APR 2006

STERN21.007APC PATENT

WORKPIECES COATED WITH AN ALUMINUM/MAGNESIUM ALLOY

[0001] The present invention is directed to workpieces coated with an aluminum/magnesium alloy and to a method for the production thereof.

[0002] Deposition of aluminum, magnesium or aluminum/magnesium alloys on workpieces consisting of base metals is a convenient way of protecting such materials from corrosion. At the same time, they are provided with a decorative coating. To this end, the protective metal layer is predominantly deposited on the workpiece by means of electroplating. The deposited metal layer significantly improves the corrosion resistance of such workpieces. However, it has been found that the corrosion resistance of a workpiece depends on the adhesion of the protective layer coated on the workpiece. In the event of insufficient adhesion of the protective layer on the workpiece, the protective layer will easily be removed, e.g. when screwing a screw constituting a workpiece and provided with a surface layer of aluminum, magnesium or aluminum/magnesium alloy into a second workpiece. This results in corrosion, especially contact corrosion, in these areas. Such corrosion will inevitably lead to destruction of the workpiece. Consequently, long-term prevention of corrosion is not ensured.

[0003] In the prior art, there have been various attempts of solving these problems.

[0004] DE 31 12 919 A1 suggests providing metal-coated iron workpieces with an adhesion-promoting intermediate layer made of cobalt, cobalt alloys or cobalt containing nickel and electroplating an aluminum layer thereon. The intermediate layer serving as adhesion promoter is electroplated from an aqueous medium. Following coating of the electro-aluminum layer on the adhesion-promoting layer, the electro-aluminum layer optionally can be chromatized. In this way, the corrosion resistance is further improved.

[0005] DE 38 04 303 suggests a method of improving the adhesion of electrodeposited aluminum layers on metal workpieces by coating an adhesion-promoting layer. A non-aqueous electrolyte is used to coat the adhesion-promoting layer of iron, iron and nickel, nickel, cobalt, copper, and alloys of the above-mentioned metals, or tin-nickel alloys. Following coating of the intermediate layer as adhesion-promoting layer on a metal workpiece, an electro-aluminum layer is coated on the intermediate layer. In doing so, it is essential to coat the intermediate layer from a non-aqueous electrolyte, because otherwise, i.e., when using an aqueous electrolyte, embrittlement of the metal workpiece will occur due to the hydrogen being formed during electrolysis. As a result, the high-strength low-alloy steels frequently being used are adversely affected. Embrittlement of the workpieces is avoided by using a non-aqueous electrolyte to coat the intermediate metallic layer.

[0006] Both DE 31 21 919 A1 and DE 38 04 303 A1 use coating of pure electro-aluminum layers on workpieces provided with an intermediate layer. Neither of the above printed documents describes coating of aluminum/magnesium alloys on workpieces.

[0007] EP 1 141 447 B1 discloses electrolytes for coating workpieces with layers of an aluminum/magnesium alloy. In particular, such coating is necessary in those cases where joints with magnesium parts are to be generated, because the corrosion products of magnesium metal are alkaline, attacking the aluminum surface coatings. By using aluminum/magnesium alloys, contact corrosion is avoided and long-term resistance of the coating is provided. What is suggested is aluminum/magnesium alloy coating of steel fastening elements intended to contact magnesium component parts, especially in the automobile industry. EP 1 141 447 B1 fails to disclose any intermediate metallic layers interposed between the workpiece and corrosion-reducing layer of aluminum/magnesium alloy.

[0008] The prior art aluminum/magnesium layers coated on a workpiece are very hard and brittle. When using fastening means provided with an aluminum/magnesium layer, e.g. screws, to fasten component parts, there is a risk in that the screws would cause superficial roughening of the component parts as a result of the aluminum/magnesium layer coated on the fastening means, destroying said parts in the worst case. In particular, such risk is

present in those cases where the component parts are made of relatively soft or brittle materials such as magnesium, for example. Again, as a result of such superficial destruction of the component part, the latter may be exposed to increased corrosion which may lead to the destruction of said component part.

[0009] However, there is also a risk in that the aluminum/magnesium layer coated on the fastening means undergoes breaking, thereby exposing the base material of the fastening means, e.g. iron or steel. Again, such exposure of the corrosion-prone base material results in increased corrosion of the fastening means through contact corrosion.

[0010] Fundamentally, the above-described corrosion frequently occurs at high pH values, so that the corrosion rate increases at high pH values in both above-mentioned cases of surface layer destruction of the fastening means or component part.

[0011] The technical object of the present invention is to provide coated workpieces which have improved corrosion resistance, particularly in the alkaline range, and exhibit reduced corrosion in combination with other materials, especially when using the coated workpieces as fastening means to fasten component parts.

[0012] The technical object of the present invention is accomplished by means of a coated workpiece comprising a substrate, an intermediate metallic layer coated on the substrate, and a layer coated on said intermediate layer, which includes an aluminum/magnesium alloy.

[0013] In a preferred embodiment the surface of the substrate is electrically conductive. In a preferred fashion, this can be achieved by coating the substrate with graphite.

[0014] The substrate preferably includes a metal and/or a metal alloy. Alternatively, the substrate can be a metallized substrate, in which case the substrate can be metallized on the entire surface or part of its surface. Preferred substrates include plastic materials.

[0015] In addition, the substrate may include constituents selected from the group of iron, steel, iron alloy, nonferrous metals, pressure-cast zinc, pressure-cast aluminum, titanium, titanium in the form of an alloy, magnesium, pressure-cast magnesium, or mixtures thereof, the above-mentioned metals preferably being present as alloy components in the substrate.

[0016] The intermediate metallic layer preferably includes iron, iron and nickel, tin and nickel, nickel, cobalt, copper, chromium, molybdenum, vanadium or alloys of the above-mentioned metals.

[0017] The intermediate metallic layer preferably has a layer thickness of from 0.1 μ m to 30 μm. In another preferred embodiment the layer thickness of the intermediate metallic layer is from 0.5 μm to 20 μm, preferably from 1 μm to 10 μm, and more preferably from 1.5 μm to 8 μm.

[0018] The layer coated on the intermediate layer, which includes an aluminum/magnesium alloy, preferably includes from 0.5 to 70 wt.-% magnesium. In a more preferred embodiment the aluminum/magnesium alloy includes from 1 to 50 wt.-%, preferably from 2 to 40 wt.-% magnesium, and in another preferred embodiment from 3 to 30 wt.-%, preferably from 4 to 25 wt.-%, and more preferably from 5 to 20 wt.-% magnesium.

[0019] The layer including an aluminum/magnesium alloy preferably has a layer thickness of from 0.1 μm to 100 μm. In another preferred embodiment the layer thickness is 0.5 μm to 70 μm, preferably 1 μm to 50 μm, preferably also 2 μm to 40 μm, more preferably 3 μm to 30 μm, preferably also 4 μm to 28 μm, with 5 μm to 25 μm being most preferred.

[0020] The layer including the aluminum/magnesium alloy preferably is the surface layer of the coated workpiece. Alternatively, at least one additional layer can be coated on said layer including the aluminum/magnesium alloy, which layer preferably is a passivation.

[0021] The coated workpieces are preferably rack goods, bulk materials, or continuous products, the coated workpiece preferably being a wire, a metal sheet, a screw, a nut, a concrete anchorage, a fastening element, or a machine component part. In a preferred fashion the coated workpiece is used in the automobile industry in the transmission, engine and bodywork sectors. It can be an oil pan or a transmission oil pan.

[0022] Another subject matter of the present invention is to provide a method for the production of a coated workpiece, comprising the steps of:

a) coating an intermediate metallic layer on a substrate, and

b) coating a layer including an aluminum/magnesium alloy on said intermediate metallic layer.

[0023] In step a), the intermediate metallic layer is preferably deposited from an aqueous solution or from a non-aqueous solution.

[0024] In a preferred embodiment the intermediate metallic layer is deposited by chemical means.

[0025] Alternatively, the intermediate metallic layer can be electrodeposited from an aqueous electrolyte in step a). Possible electrolytes are solutions of metal salts of iron, cobalt, nickel, copper or tin. They can be present in the form of halides, sulfates, sulfonates or fluoborates. The electrolytes may contain further additives such as complexing substances.

[0026] Alternatively, the intermediate metallic layer can also be electrodeposited from a non-aqueous electrolyte in step a). Possible electrolytes contain compounds of molybdenum or vanadium or any other of the metals mentioned above which can be included in the intermediate layer. The metals are preferably in the form of halides which can be complexed or reacted with ether, especially diethyl ether, and/or acetylacetonate (acac) to form the corresponding metal acetylacetonates.

[0027] In step b), the layer including an aluminum/magnesium alloy is preferably deposited from an anhydrous electrolyte. In another preferred embodiment the layer includ-

ing an aluminum/magnesium alloy is preferably electrodeposited from an anhydrous electrolyte in step b). Any electrolyte known to those skilled in the art can be used as electrolyte. More specifically, the electrolyte includes organoaluminum compounds of general formulas (I) and (II):

$$M[(R^1)_3Al\text{-}(H\text{-}Al(R^2)_2)_n\text{-}R^3] \qquad \text{(I)}$$

$$Al(R^4)_3 \qquad \text{(II)}$$

wherein n is equal to 0 or 1, M is sodium or potassium, and R^1, R^2, R^3, R^4 can be the same or different, R^1, R^2, R^3, R^4 being a C_1-C_4 alkyl group, and a halogen-free, aprotic solvent being used as solvent for the electrolyte.

[0028] A mixture of $K[AlEt_4]$, $Na[AlEt_4]$ complexes and $AlEt_3$ can be employed as electrolyte. The molar ratio of complexes to $AlEt_3$ is preferably from 1:0.5 to 1:3, more preferably 1:2.

[0029] Electrolytic deposition on the workpiece of the layer including an aluminum/magnesium alloy is performed using a soluble aluminum anode and a likewise soluble magnesium anode, or using an anode made of an aluminum/magnesium alloy.

[0030] Electrolytic coating is preferably performed at a temperature of from 80 to 105 °C. Preferred is an electroplating bath temperature of from 91 to 100°C.

[0031] In a preferred embodiment an electrically conductive layer is coated on the substrate prior to coating the intermediate metallic layer in step a).

[0032] The electroconductive layer can be coated on the substrate using any method known to those skilled in the art. In a preferred fashion the electrically conductive layer is coated on the substrate by means of metallization.

[0033] Unexpectedly, there is no impairment of the coated workpiece when using the coated workpiece of the present invention as fastening means. Although the surface layer of

an aluminum/magnesium alloy is very hard, brittle and sparingly ductile, the coating still adheres very tightly to the coated workpiece during and after use as fastening means. Furthermore, the coating being used, consisting of the intermediate layer and the surface layer, is flexible to such an extent that it is not adversely changed following use as fastening means. When the coated workpiece, e.g. in the form of a screw, is screwed into a component part, the surface treatment of the workpiece unexpectedly backs away, resulting in a further reduction of strain on the coated workpiece. Because no damage is done to the intermediate metallic layer and the surface layer including an aluminum/magnesium alloy, the coated workpiece is reliably protected from corrosion, especially contact corrosion, even after and during use thereof.

[0034] Prior art workpieces provided with an aluminum/magnesium coating fail to offer the advantages mentioned above. The surface layer, which consists of an aluminum/magnesium layer, either is destroyed, so that the workpiece will undergo corrosion, or the very hard and brittle layer of aluminum/magnesium alloy of prior art workpieces destroys the surface of the component parts to be fastened, so that the latter are subsequently exposed to increased corrosion.

[0035] The invention will be illustrated in more detail with reference to the following examples.

EXAMPLES:

Example 1

[0036] A sheet of St37 steel 100 × 25 × 1 mm in size is provided with a nickel intermediate layer having a thickness of about 1 μm. The nickel layer is electrodeposited from an aqueous nickel sulfamate electrolyte. Thereafter, a layer of an aluminum/magnesium alloy with a magnesium content of 20 wt.-% and a layer thickness of 12 μm is deposited on the nickel layer from a non-aqueous electrolyte by means of electroplating. The coated metal sheet is bent lengthways by an angle of 180°, and the coated metal layers remain intact in the area of the bending edge.

Comparative Example 1

[0037] A sheet of St37 steel 100 × 25 × 1 mm in size is provided with a layer of an aluminum/magnesium alloy with a magnesium content of 20 wt.-% and a layer thickness of 12 μm by means of electrodeposition from a non-aqueous electrolyte. The metal sheet thus coated is bent lengthways by an angle of 180°, during which process the coating is partially disrupted along the bending edge, partially undergoing flaking in the form of ultrafine needles.

Example 2

[0038] Five M6 × 55 size screws are provided with an aluminum/magnesium alloy with a magnesium content of 15 wt.-% and a layer thickness of 16 μm by means of electrodeposition from a non-aqueous electrolyte.

[0039] Five additional M6 × 55 size screws are provided with a nickel layer having a layer thickness of about 1 μm. The nickel layer is electrodeposited from an aqueous nickel sulfamate electrolyte. Thereafter, a layer of an aluminum/magnesium alloy with a magnesium content of 15 wt.-% and a layer thickness of 16 μm is deposited on the nickel layer from a non-aqueous electrolyte by means of electroplating.

[0040] All screws are screwed half-way into a nut of corresponding size and subsequently unscrewed. Thereafter, the screws thus treated are suspended in a salt spray chamber and investigated for their corrosion behavior. As can be seen, screws provided with a nickel intermediate layer take a longer time until initial corrosion of the screws can be observed.

Example 3

[0041] M5 × 5 size screws are electroplated with an aluminum/magnesium alloy with a magnesium content of 10 wt.-% and an average layer thickness of 14 μm from a non-aqueous electrolyte in a drum.

[0042] Additional screws are provided with a nickel intermediate layer having a layer thickness of about 1-2 μm of nickel. The nickel layer is electrodeposited from an aqueous nickel sulfamate electrolyte. Thereafter, a layer of an aluminum/magnesium alloy with a magnesium content of 10 wt.-% and an average layer thickness of 15 μm is electrodeposited on the nickel layer from a non-aqueous electrolyte in a drum.

[0043] Three equally coated screws each time are fully screwed into a casing made of an aluminum/magnesium alloy which has a self-retained nut matching the screw diameter. Thereafter, the corrosion behavior is investigated in a salt spray chamber. As can be seen, the casings having screws with an intermediate layer of nickel screwed therein undergo corrosion significantly later. The casings having screws with no nickel intermediate layer show initial corrosion phenomena at an earlier point in time.

[0044] In summary, the examples specified above indicate that the intermediate metallic layer causes a significant improvement of the corrosion resistance. Coated workpieces comprising a substrate, an intermediate metallic layer coated on the substrate, and a layer coated on said intermediate layer, which includes an aluminum/magnesium alloy, show a superior pattern of properties which is not seen in prior art workpieces.